Journal of Organometallic Chemistry, 102 (1975) 175—183

SYNTHESIS OF α-METHYLENE-γ-BUTYROLACTONE VIA TRANSITION METAL CARBENE COMPLEXES

CHARLES P. CASEY* and WILLIAM R. BRUNSVOLD
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)
(Received June 3rd, 1975)

Summary

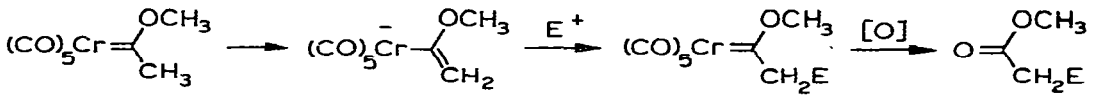
The anion of (2-oxacyclopentylidene)pentacarbonylchromium(0), (I), is alkylated by addition to $ClCH_2OCH_3$ to give (5-methoxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0), (VI), and (5,5-dimethoxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0), VII, in 45 and 13% yields, respectively, as well as (5-hydroxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0), (VIII), and (5-hydroxymethyl-5-methoxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0), (IX), in a combined yield of 18%. Methanol and water are eliminated from VI and VIII, respectively, to give 64% of (5-*exo*-methylene-2-oxacyclopentylidene)pentacarbonylchromium(0), (IV), which affords 76% α-methylene-γ-butyrolactone, (X), upon oxidation by ceric ion. Direct addition of one-half equivalent of $ClCH_2OCH_3$ to the anion of I gave a 74% yield of the methylene bridged dimer V. Addition of excess $ClCH_2OCH_3$ to the bis(triphenylphosphine)iminium salt of the anion of I gave primarily VI (38%).

Introduction

In our efforts to develop transition metal carbene complexes into useful reagents for organic synthesis, we have found ways of elaborating the structure of carbene complexes via reactions of "carbene anions" [1-3] and have found means of releasing the carbene ligand from the metal complex by oxidation to esters [4] or by reaction with diazomethane or phosphorus ylides to give vinyl ethers [4,5].

Carbanions can be conveniently generated α to the carbene carbon atom of transition metal carbene complexes by treatment with n-BuLi [2,7] or NaOMe [6]. These carbene anions are moderately reactive toward aldehydes, acid chlorides, epoxides, and reactive alkylating agents such as methyl fluorosulfonate and α-bromoesters [1,2,3]. The carbene anions do not react with esters, ketones, or

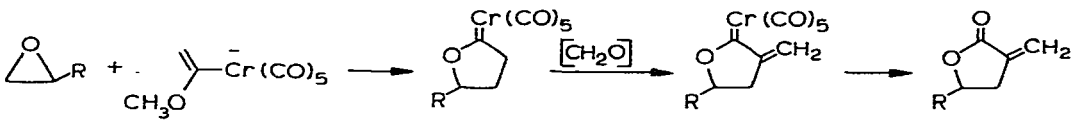
alcohols and consequently protecting groups are not required for these functionalities. The carbene complexes are among the most acidic neutral carbon acids known: in THF, $(CO)_5CrC(OCH_3)CH_3$ and p-HOC_6H_4CN are equally strong acids [7]. Thus carbene anions may serve as mild and selective reagents for introduction of new carbon atoms into an organic structure.



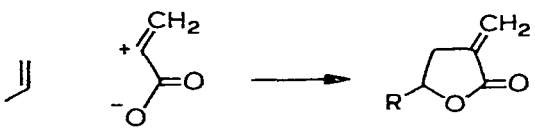
Here we report our efforts to use metal carbene complexes for the synthesis of α-methylene-γ-butyrolactones [8-10]. The α-methylene-γ-butyrolactone unit is a key structural feature in many compounds of high physiological activity. In vivo antitumor activity has been shown for the polyfunctional α-methylene-γ-butyrolactones vernolepin, euratopin acetate, and elephantophii the α-methylene-γ-butyrolactone unit is essential for cytotoxic activity [11,12]. The chemical synthesis of these sesquiterpene lactones will require mild and specific reagents for the introduction of the α-methylene-γ-butyrolactone unit. Here we have explored the feasibility of synthesizing polyfunctional α-methylene-γ-butyrolactones using several new reactions of transition metal carbene complexes which we recently discovered.

Our proposed synthetic route is shown in Scheme 1. Carbene anions are

SCHEME 1

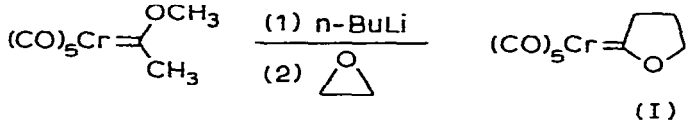


known to react at the least substituted carbon of an epoxide to give 2-oxacyclopentylidene complexes. The resulting carbene complex possesses an active methylene unit capable of further reaction with formaldehyde to give an *exo*-methylene functionality. Finally, oxidation of the elaborated carbene complex would give the desired substituted α-methylene-γ-butyrolactone. The overall synthetic sequence is the equivalent of the dipolar addition shown below.



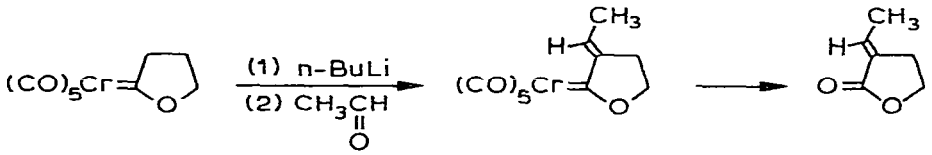
Results and discussion

The conjugate base of (methylmethoxycarbene)pentacarbonylchromium(0) was condensed with ethylene oxide as reported previously to give (2-oxacyclopentylidene)pentacarbonylchromium(0), (I) [1]. The reaction of the conjugate base of I with acetaldehyde was studied as a model for the reaction with form-



(I)

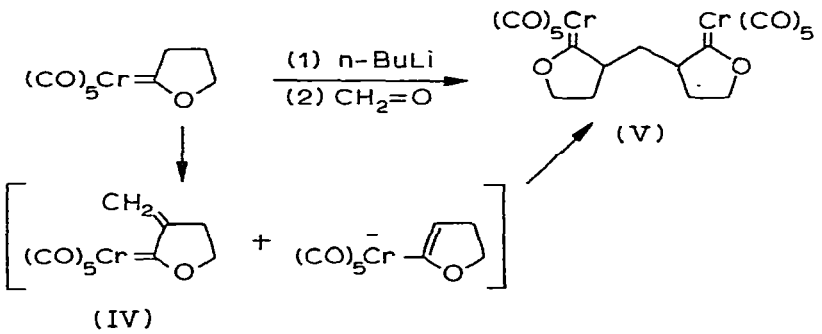
aldehyde. Treatment of the anion of (I), generated in THF at —78°C with 1.2 equiv. n-BuLi, with acetaldehyde gave the condensation product, (II *E*), isolated in 28% yield as a bright red solid. The stereochemistry of the condensation prod-



(I) (II *E*) (III *E*)

uct was assigned the *E*-configuration on the basis of oxidative cleavage to lactone (III *E*) whose structure was assigned on the basis of NMR data (see experimental).

Direct condensation of the conjugate base of I with either aqueous or gaseous formaldehyde failed to produce the *exo*-methylene carbene complex (IV). The only product isolated was the carbene complex dimer V. The dimer V could arise from Michael addition of the carbene anion of I to an initially formed *exo*-methylene carbene complex IV.

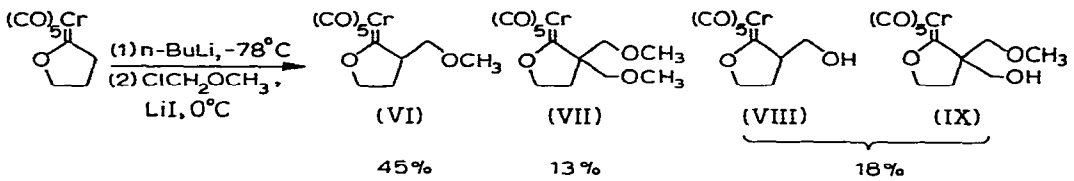


(V)

(IV)

In view of our failure to isolate IV from direct condensation of the anion of I with formaldehyde, we investigated the reactions of the conjugate base of I with several synthetic equivalents of formaldehyde. Attempted reaction with diiodomethane led only to re-isolation of I. Reaction of the conjugate base of I with $ClCH_2OCH_3$ proved more successful. Addition of 0.82 equiv. n-BuLi (0.95 equiv. total base) to I in THF at —78°C gave a pale yellow solution which was warmed to 0°C and added dropwise to 1 equival. LiI and 11 equival. $ClCH_2OCH_3$ in THF at 0°C to give an orange solution. Preparative thin-layer chromatography (prep TLC) gave three bands. The fastest moving band afforded a 33% recovery of I. The middle band consisted of a mixture of (5-methoxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0) (VI) and (5,5-dimethoxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0) (VII), in 45 and 13% yields, respectively, based on recovered I. The slow moving band contained an 18% yield of about a 60/40 mixture of (5-hydroxymethyl-2-oxacyclopentylidene)-

pentacarbonylchromium(0) (VIII) and (5-hydroxymethyl-5-methoxymethyl-2-oxacyclopentylidene)pentacarbonylchromium(0) (IX). Compounds VIII and IX could not be separated by prep TLC but parent ions for each were observed in the mass spectrum.



Since VI could be converted to the *exo*-methylene carbene complex IV by loss of MeOH, an attempt was made to optimize the yield of VI by variation of the reaction conditions (Table I). Polyalkylation of I gave VII and IX in addition to the desired monoalkylation product, VI, and was a severe problem. Polyalkylation could be reduced by running the reaction under conditions where the anion of I was quenched immediately by rapid reaction with $ClCH_2OCH_3$. Thus, slow inverse addition of the anion of I to an excess of $ClCH_2OCH_3$ and LiI proved most successful. One equivalent of LiI was required to obtain good yields of VI. Without LiI only VII and the dimer V are formed. Apparently, LiI reacts with $ClCH_2OCH_3$ under the reaction conditions to give the more reactive alkylating agent ICH_2OCH_3. Best results were obtained in THF at 0°C since no reaction was observed in Et_2O. At 25°C in THF the ratio of monoalkylated VI to dialkylated VII increased but the yield of VI was lower. Direct addition of the alkylating agent to the anion of I gave mostly dialkylated VII and dimer V. Excess base resulted in a lower ratio of mono-to dialkylation but lowering the amount of base gave a larger amount of recovered I so a medium range of 0.95 to 1.1 equivalents total base was desired. The reaction at 25°C appears to be complete within 10 min after the anion has been added since there is little change in product ratio or amount of products after 10 to 20 min.

The ease of dialkylation α to the carbene carbon could be attributed to a similar reactivity of the conjugate bases of I and VI. The problem of dialkylation in these systems is currently under extensive investigation.

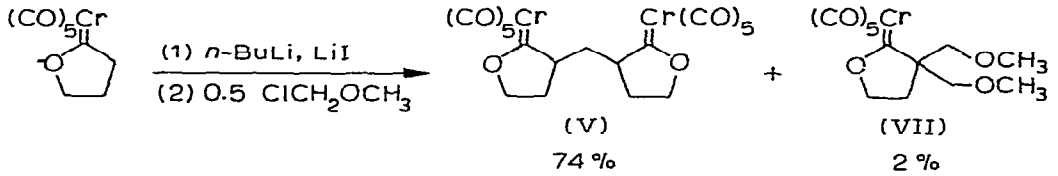
TABLE I

REACTION OF I WITH $ClCH_2OCH_3$

Number of equivalents				T(°C)	t (min)	Yield (%)					
I	Total base	LiI	$ClCH_2OCH_3$			I	VI	VII	VIII + IX[a]	V	Σ
1	0.9	0	11.5	0	10	37		23		13	73
1	1.2	1.0	11.5	0	20	20	17	22	19		78
1	1.0	1.0	11.5	0	20	26	20	20	13		79
2	0.95	1.0	11.5	0	20	33	30	9	13		85
2	1.1	1.0	11.5	0	20	28	26	8	21		83
2	0.95	1.0	5.0	25	20	38	21	3	13		75
2	0.95	1.0	11.5	25	20	28	25	4	21		78
2	0.95	1.0	11.5	25	10	34	25	2	12		73

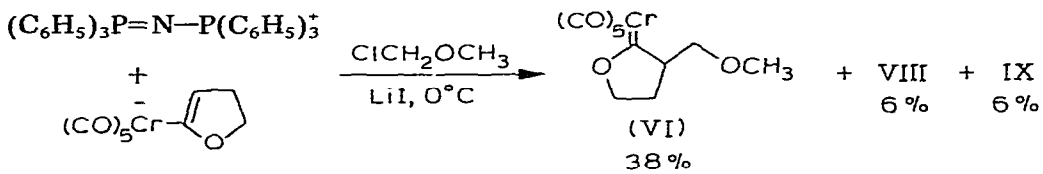
[a] 60/40 mixture.

The methylene-bridged dimer V was isolated in 74% yield by adding 0.5 equivalent of $ClCH_2OCH_3$ to a THF solution of the anion of I at 0°C generated from one equivalent of n-BuLi and containing 1 equivalent of LiI.



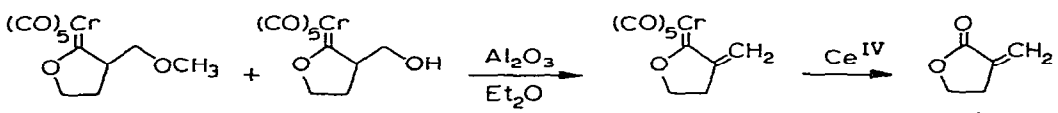
(V) 74 % (VII) 2 %

The addition of five equivalents of $ClCH_2OCH_3$ to a THF solution containing LiI and the bis(triphenylphosphine)iminium salt of the anion of I afforded I (35% recovery) and VI (38% based on recovered I). No dialkylated VII was seen by NMR. However, VIII and IX were formed in about equal amounts in a combined yield of 12%.



(VI) 38 %

Elimination of methanol from VI would give the desired exomethylene carbene complex IV. Attempts at acid and base catalyzed eliminations from homogeneous reaction mixtures failed. However, treatment of an ether solution of VI at 25°C for 1 h with basic Al_2O_3 led to smooth elimination of MeOH and formation of IV in 71% yield*. A mixture of VI, VII, VIII, and IX from prep TLC was treated with Al_2O_3 in Et_2O at 25°C to effect elimination of MeOH and H_2O from VI and VIII, respectively, to give 64% of IV based on VI and VIII. Carbene complex IV was separated from VII and IX by prep TLC and characterized by NMR, IR, and mass spectral data.



(VI) (VIII) (IV) 64% (X) 76%

Finally, oxidative cleavage of the *exo*-methylene carbene complex IV with ceric ion in acetone gave a 76% yield of *exo*-methylene-γ-butyrolactone (X). The synthesis of α-methylene-γ-butyrolactone reported here demonstrates the utility of metal—carbene complexes in organic synthesis. In particular, the mild reaction conditions employed are indicative of the promising nature of these reagents. However, the low to moderate yields obtained in several of the reactions and the problems with dialkylation of carbene anions presently detract from the inherent attractiveness of these reactions. Hopefully, our current research aimed at improving yields and avoiding dialkylation will help to solve these problems.

* We thank Prof. A.I. Meyers for suggesting this procedure.

Experimental section

NMR spectra were taken using a JEOLCO MH-100 spectrometer. Infrared spectra were recorded on a Perkin—Elmer 267 Infrared spectrophotometer. Mass spectra were taken using an AEI-902 mass spectrometer. Gas chromatographic analyses were performed using a Hewlett—Packard Model 5700A gas chromatograph. Preparative thin-layer chromatography (prep TLC) was performed on Merck PF 254 silica gel. All reactions were carried out under a nitrogen atmosphere. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under a nitrogen atmosphere. Carbene complex I was prepared according to the procedure of Casey and Anderson in 58% yield [1]. The Al_2O_3 used in the preparation of IV was Al_2O_3 PF 254 (Type *E*) purchased from Matheson Scientific, Inc.

[5-(E-ethylidene)-2-oxacyclopentylidene] pentacarbonylchromium(0) (II)

n-Butyllithium (0.44 ml, 1.68 *M*, 0.73 mmol) was added to I (170 mg, 0.65 mmol) in 15 ml of THF at —78°C. Acetaldehyde (46 mg, 0.80 mmol) was injected and the pale yellow solution became light orange. After 45 min at —78°C, HCl/Et_2O (0.82 ml, 2.07 *M*, 1.70 mmol) was added to give a red solution. Prep TLC (hexane) afforded II (52 mg, 28%, R_f = 0.30) as a red solid, m.p. 82-5°C, exact mass, 287.9719 (calcd. for $C_{11}H_8O_6Cr$, 287.9725). NMR (CS_2) δ 2.07 (d of t, *J* = 2, 7 Hz, 3H, CH_3), 2.64 (broad t, 2H, CH_2CH_2O), 4.87 (t, *J* = 7 Hz, 2H, CH_2O), 7.36 (mult., 1H, vinyl H). IR (hexane) ν(CO) 2063w, 1987w, 1957s, 1945s. UV (hexane) λ_{max} 233 mμ (ε = 36,800), 467 mμ (ε = 5,800). Compound II was also characterized by ceric ion oxidation to α-(*E*-ethylidene)-γ-butyrolactone (III *E*), whose IR and NMR spectra were superimposable on those of an independently synthesized sample.

α-(E-ethylidene)-γ-butyrolactone 3-E

α-Diethylphosphonate-γ-butyrolactone [13] (6 g, 27 mmol) was added dropwise to a mixture of NaH (1.15 g, 27 mmol) and 50 ml of Et_2O at 0°C to give a white precipitate after 30 min. Acetaldehyde (1.01 g, 22.8 mmol) was added dropwise at 0°C to give a cream colored precipitate. After 10 min of stirring at 0°C and 30 min at 25°C, 25 ml of H_2O was added. The Et_2O phase was washed twice with 10 ml of H_2O and dried (Na_2SO_4). The Et_2O was removed and the residue distilled. The fraction with b.p. 42°C/0.1 mm afforded 0.64 g of a mixture of the *E* and *Z* isomers of α-ethylidene-γ-butyrolactone and some $P(OEt)_3$. Prep TLC (1/1; hexane/$CHCl_3$) resulted in two bands. The faster moving band (R_f = 0.33) afforded *Z*-(α-ethylidene)-γ-butyrolactone (III *Z*) as an oil. NMR ($CDCl_3$) δ 2.19 (d of t, *J* = 2.5, 7.5 Hz, 3H, CH_3), 2.92 (t of quintets, *J* = 2.5, 7.5 Hz, 2H, CH_2CH_2O), 4.33 (t, *J* = 7.5 Hz, 2H, CH_2O), 6.36 (t of quartets, *J* = 7.5, 2.5 Hz, 1H). IR (neat) 1755 (C=O), 1672, 1442, 1377, 1210, 1120, 1026, 959, 860 cm^{-1}. The slower moving band (R_f = 0.25) gave III *E* as an oil which was contaminated with $P(OEt)_3$. Pure III *E* was obtained by prep. GLC (5′ × 1/4″ 10% UCON LB-550X column, 150°C). The retention time of III *E* (11 1/2 min) was longer than that of III *Z* (8 min). III *E* NMR ($CDCl_3$) δ 1.85 (d of t, *J* = 2, 7 Hz, 3H, CH_3), 2.86 (mult, 2H, CH_2CH_2O), 4.38 (t, *J* = 7.5 Hz,

2H, CH_2O), 6.82 (mult., 1H). IR (neat) 1756 (C=O), 1682, 1375, 1220, 1132, 1035, 1011, 989, 716 cm^{-1}.

The key points in assigning the structures of III *Z* and III *E* were the chemical shifts of the H and CH_3 groups of the *exo*-ethylidene group. The carbonyl oxygen atom deshields the CH_3 of III *Z* relative to III *E* by 0.34 ppm; similarly the carbonyl oxygen deshields the H of III *E* relative to III *Z* by 0.46 ppm. Similar deshielding effects of α,β-unsaturated ketones have been observed previously [14].

Reaction of the anion of I with formaldehyde

n-Butyllithium (0.24 ml, 1.58 *M*, 0.38 mmol) was added to I (100 mg, 0.38 mmol) in 10 ml of THF at —78°C. A 37% formaldehyde solution (0.14 ml, 0.56 mmol, 37% formaldehyde, 10% MeOH, 53% H_2O) was added and the solution stirred at 25°C for 1 h. Prep TLC (hexane) gave only V (28 mg, 28%, R_f = 0.05) as an orange solid, m.p. 126-9°C NMR ($CDCl_3$) δ 1.9-2.2 (mult., 6H, bridging CH_2 and CH_2CH_2O), 3.64 (mult., 2H, methine H's), 5.00 (t, J = 7 Hz, 4H, CH_2O); IR (hexane) ν(CO) 2068, 1996, 1989, 1970, 1965, 1955, and 1923 cm^{-1}. The large number of bands can be attributed to the presence of 2 diastereomers; exact mass, 535.9110 (calcd. for $C_{19}H_{12}O_{12}Cr_2$, 535.9137). UV (EtOH) λ_{max} 239 mμ (ϵ = 38,300), 375 mμ (ϵ = 8,900). Analysis found: C, 42.55; H, 2.34; Cr, 19.20. . ($C_{19}H_{12}O_{12}Cr_2$) Calcd.: C, 42.54; H, 2.26; Cr, 19.38%.

In a similar experiment the anion of I was generated from I (125 mg, 0.48 mmol) and n-BuLi (0.27 ml, 1.75 *M*, 0.48 mmol) at —78°C. The solution was warmed to 25°C and gaseous formaldehyde was led into the solution in a stream of N_2. Formaldehyde was generated by heating paraformaldehyde (162 mg, 1.8 mmol) to ~140°C in a separate flask which was connected to the reaction flask by a glass tube. After 10 min, the paraformaldehyde had disappeared and the reaction solution became orange. Prep TLC (5/1 hexane/Et_2O) gave only V (18 mg, 14%, R_f = 0.10) identified by NMR.

Reaction of the anion of I with 0.5 equivalent $ClCH_2OCH_3$

The anion of I was generated by injecting n-BuLi (0.50 ml, 1.60 *M*, 0.80 mmol) into 10 ml of a THF solution at —78°C containing I (200 mg, 0.76 mmol) and LiI (58 mg, 0.43 mmol). The solution was warmed to 0°C and $ClCH_2OCH_3$ (32 μl, 0.42 mmol) was injected into the solution. After 20 min, the THF was removed and prep TLC (2/1 hexane/Et_2O) allowed the isolation of I (7 mg, 3.5%, R_f = 0.25), V (152 mg, 74%, R_f = 0.05), and VII (5 mg, 2%, R_f = 0.22) as a yellow solid.

VII: m.p. 46-8°C. NMR ($CDCl_3$): δ 2.19 (t, J = 7.5 Hz, 2H), 3.31 (s, 6H, OCH_3), 3.55 (d, J = 9 Hz, 2H, 1/2 of AB quartet, $\underline{CH_2}OCH_3$), 3.95 (d, J = 9 Hz, 2H, 1/2 of AB quartet, $\underline{CH_2}OCH_3$), 4.96 (t, J = 7.5 Hz, 2H, $CH_2\underline{CH_2}O$). IR (hexane) ν(CO) 2066, 1990, 1955, 1926, and 1918 cm^{-1}. Exact mass: 350.0105 (calcd. for $C_{13}H_{14}O_8Cr$: 350.0092). UV (hexane) λ_{max} 240 mμ (ϵ = 23,600), 383 mμ (ϵ = 6,800).

Reaction of the PPN salt of the α-anion of [I] with $ClCH_2OCH_3$

The bis(triphenylphosphine)iminium (PPN) salt of Ia was prepared in 76% yield according to the method used in the preparation of the PPN salt of the

α-anion of (methylmethoxycarbene)pentacarbonylchromium(0) [7]. The PPN salt of Ia (214 mg, 0.268 mmol) and LiI (36 mg, 0.268 mmol) were dissolved in 2 ml of THF at 0°C, $ClCH_2OCH_3$ (105 μl, 1.34 mmol) was injected, and the solution stirred 15 min at 0°C. A white solid, PPN^+Cl^-, precipitated and the solution became orange. 20 ml of Et_2O was added and the solution removed by cannula. Removal of solvent and prep TLC (hexane) gave I (25 mg, 35%, R_f = 0.16), VI (21 mg, 38% based on recovered I, R_f = 0.08), and about a 1/1 mixture of VIII and IX (8 mg, 12% based on recovered I, R_f = 0.0). None of VII was seen by NMR. Compound VI was an orange oil. NMR ($CDCl_3$) δ 2.00 (mult., 2H, CH_2-CH_2O), 3.35 (s, 3H, OCH_3), 3.6-4.0 (mult., 2H, methine H and 1 of 2 diastereotopic H's of CH_2OCH_3), 4.12 (d of d, J = 5.9 Hz, 1H, 1 of 2 diastereotopic H's), 4.96 (t, J = 8 Hz, 2H, CH_2O). IR (hexane) ν(CO) 2069, 1993, 1963, 1957, 1935 cm^{-1}. Exact mass: 305.9824 (calcd. for $C_{11}H_{10}O_7Cr$: 305.9830).

Reaction of the α-anion of I with excess $ClCH_2OCH_3$

n-Butyllithium (0.22 ml, 1.61 *M* total base, 0.36 mmol) was injected into a solution of I (100 mg, 0.38 mmol) in 5 ml of THF at —78°C. The pale yellow solution was warmed to 0°C and transferred dropwise by cannula over a 10 minute period into 2 ml of THF at 0°C containing LiI (51 mg, 0.38 mmol) and $ClCH_2OCH_3$ (350 μl, 4.4 mmol). The resulting orange solution was stirred another 20 min at 0°C.

Prep. TLC (two elutions with hexane) gave three bands. The yellow band at R_f = 0.20 yielded 33 mg (33%) of I. The orange band (R_f = 0.11) gave 47 mg of an orange oil consisting of VI and VII in 45 and 13% yields, respectively, based on recovered I. The lower yellow band (R_f = 0.05) afforded 17 mg (13%) of a 3/2 mixture of VIII and IX.

In a larger scale experiment starting with 300 mg I, greater amounts of the mixture of VIII and IX were obtained from prep TLC (hexane). The mixture of VIII and IX was rechromatographed on prep TLC (Et_2O). A yellow band (R_f = 0.25) yielded 35 mg of VIII as an orange oil contaminated by small amounts of IX. An orange band (R_f = 0.35) yielded 25 mg of IX as an orange oil contaminated by small amounts of VIII.

Peaks attributed to VIII in the IR (hexane) occurred at 2067w, 1991w, 1966s, 1951s, and 1938s cm^{-1}. The NMR of VIII consisted of resonances at δ 1.58 (broad s, 1H, OH), 2.06 (mult, 2H, $\underline{CH_2}CH_2O$), 3.6-4.5 (broad mult, 3H, $\underline{CH}$ and $\underline{CH_2}OH$), and 4.96 (mult, 2H, CH_2O). Mass spec: parent at *m/e* = 292.

Peaks attributed to IX in the IR (hexane) occurred at 2065w, 1991w, 1966s, 1955s, and 1933w, (sh) cm^{-1}. The NMR of IX consisted of resonances at δ 2.1 (mult, 2H, $\underline{CH_2}CH_2O$), 3.36 (s, 3H, OCH_3), 3.8-4.3 (broad mult, 4H, $\underline{CH_2}$-OH and CH_2OCH_3), 5.0 (mult, 2H, CH_2O). In addition, a multiplet attributed to an impurity occurred at δ 4.7-4.8. Mass spec: parent at *m/e* = 336.

(5-exo-methylene-2-oxacyclopentylidene)pentacarbonylchromium(0) (IV)

Al_2O_3 (600 mg, 5.91 mmol) was added to 15 ml of Et_2O containing VI (92 mg, 0.30 mmol) and 45 mg of a 3:2 mixture of VIII and IX (0.092 mmol of VIII). A red color quickly developed and after 1 h at 25°C the solution was filtered and the solvent removed. Prep TLC (2/1 hexane/Et_2O) gave IV as a deep red solid (67 mg, 64%, R_f = 0.20). M.p. 83-84°C. NMR ($CDCl_3$) δ 2.75 (t of t, J

= 2.5, 7.5 Hz, 2H), 4.87 (t, J = 7.5 Hz, 2H, CH_2O), 6.27 (t, J = 2.5 Hz, 1H, vinyl H), 6.63 (t, J = 2.5 Hz, 1H, vinyl H). IR (hexane) ν(CO) 2066, 1991, 1964, 1952 cm^{-1}. Exact mass: 273.9559 (calcd. for $C_{10}H_6O_6Cr$: 273.9568).

Alternatively, pure VI (48 mg, 0.157 mmol) obtained from the reaction of the PPN salt with $ClCH_2OCH_3$ and Al_2O_3 (200 mg, 1.97 mmol) were combined in 10 ml of Et_2O at 25°C and stirred 45 min to afford IV (30 mg, 71%) after prep TLC.

α-Methylene-γ-butyrolactone (X)

Ceric ammonium nitrate (275 mg, 0.504 mmol) was added to IV (46 mg, 0.168 mmol) in 10 ml of acetone and the reaction mixture was stirred for 1 min. Acetone was removed under vacuum and the residue was worked up with ether and water. The ether solution contained α-methylene-γ-butyrolactone (X) (76% by gas chromatography, 20″ × 1/8″ 10% UCW-98 column, C_{11} internal standard) which was isolated by prep TLC (1/1 hexane/Et_2O, R_f = 0.22) and identified by comparison of its IR and NMR spectra with those of an authentic sample [8].

Acknowledgment

This research was supported by the National Science Foundation (Grant GP-32160 and GP-41259X).

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